

Voltammetric monitoring of gamma radiolytic degradation of phenols

Safeer Ahmed · Muhammad Ahmad ·
Shahid Bilal Butt · Ihsanullah Afghani ·
Mohammad Iqbal

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Abstract Phenol and its three chloro derivatives were electrooxidized on glassy carbon electrode under optimized conditions of concentration, number of repeated scans, scan rate, and pH of the medium. Next, the aqueous solutions of the phenols were degraded under controlled dose of gamma (γ) radiations in the range of 1–5 kGy. The post γ -irradiated phenols were investigated by cyclic voltammetry (CV) and the response was quantitated in terms of radiolytic yields (G values) and degradation efficiencies. The calculated theoretical charge densities were also in support of phenols degradation via hydroxyl radical attack. The proposed use of CV as a new monitoring method for the degradation of organic pollutants was validated with the well-established HPLC method.

Keywords Phenols · Cyclic voltammetry · Electrooxidation · Gamma radiolysis · G values · HPLC

Abbreviations

CV Cyclic voltammetry
EC Electrochemical

ET Electron transfer
BRB Britton–Robinson buffer
GCE Glassy carbon electrode
HPLC High performance liquid chromatography
SEM Scanning electron microscopy
AOP Advanced oxidation processes

1 Introduction

The water bodies and the groundwater sources are being polluted by toxic compounds due to the rapid industrial growth and anthropogenic activities. The contamination of these water bodies with hazardous pollutants ultimately results into around 14,000 deaths daily in the world [1, 2]. Phenols and its derivatives, especially the chloro and nitro substituted, have been declared to be hazardous persistent organic pollutants [3]. These contaminated effluents are being discharged from a number of industrial processes, such as oil refineries, plastic and paper industries, synthetic chemicals, pesticides, petrochemicals, pharmaceuticals, preservatives, resins, beverage, and tannery [4–6]. Many international regulatory authorities including US environmental protection agency and the European Union have declared chlorophenols (CPs) and nitrophenols as the priority pollutants [7, 8]. Therefore, the development of fast, cost effective, and efficient methods to get rid of these pollutants is one of the most exigent research topics in the field of environmental sciences.

The techniques used for the degradation of these pollutants are broadly classified into conventional methods and advanced oxidation processes (AOPs) [8], which vary with respect to their degrading efficiencies and scope. Among these, AOPs are the promising and effective

S. Ahmed (✉) · M. Ahmad
Department of Chemistry, Quaid-i-Azam University,
Islamabad 45320, Pakistan
e-mail: safeerchem@yahoo.com; safeerad@qau.edu.pk

S. B. Butt
Central Analytical Facility Division, PINSTECH,
P.O. Nilore, Islamabad, Pakistan

I. Afghani
Nuclear Institute for Food and Agriculture (NIFA),
Peshawar, Pakistan

M. Iqbal
Physics Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan

methods, for the efficient removal of the organic pollutants normally present in the potable and waste water [9–11]. Gamma (γ) radiolysis using Co-60 source is one of the most efficient AOPs and has certain advantages over other technologies, especially at industrial scale. The γ -radiolysis of water by Co-60 source produces reducing aqueous electrons and oxidizing hydroxyl radicals that are highly reactive and are proficient to degrade the organic pollutants into harmless species [12].

Electrooxidation of different phenolic pollutants have been studied under different conditions [13–15]. This study focuses on the potential usage of cyclic voltammetry (CV) to monitor the radiolytic degradation of pre and post γ -irradiated aqueous phenols while measuring the extent of eradication. The obtained CV data in terms of radiolytic yields (G values) and degradation efficiencies were complemented by the well-celebrated HPLC method. To our best information, this is the first report where CV has been used to monitor the radiolytic degradation of phenols. The proposed technique will be used as an additional efficient tool for the aforementioned analysis besides to the existing spectrophotometry, and HPLC methods. Further, CV can also provide added knowledge about the product if it is electroactive. The findings persuade that the results can be modeled to be applied to actual samples for the bulk electrolysis. In addition, some theoretical calculations were also conducted to envisage the degradation mechanism through OH radicals.

2 Experimental

2.1 Chemicals

Phenol, 2-CP, 3-CP, 2,4,6-trichlorophenol (TCP), $\text{Na}_2\text{H-PO}_4 \cdot 2\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, and citric acid 98–99 % were from Merck, Germany. Sodium hydroxide, boric acid, acetic acid, 98–99 %, and phosphoric acid 85 % were from Riedel-de-Haën, Germany. LiClO_4 , from BDH, UK and NaNO_3 from STEDEC were used as such. All solutions were prepared in deionized water.

2.2 Cyclic voltammetry

CV measurements were carried out using Eco Chemie Autolab PGSTAT 302 potentiostat/galvanostat Utrecht, The Netherlands along with the software GPES 4.9. The electrochemical (EC) studies of phenols before and after degradation were performed at room temperature 25 °C using the procedure mentioned elsewhere [16]. A Britton–Robinson buffer (BRB) containing each component acid (boric, acetic, and phosphoric acid) 0.04 mol L^{-1} and its pH adjusted 2–12 with NaOH was used as the background

electrolyte. The working electrode was glassy carbon electrode (GCE, 0.071 cm^2) from BAS, USA, while the reference and counter electrodes were saturated calomel electrode (SCE) and Pt wire, respectively. The glassy carbon was selected as working electrode due to its optimum potential window particularly in oxidative mode, high sensitivity, and extensive use for phenols in the literature.

2.3 Gamma radiolysis

Irradiation of the standard phenols solution was carried out at the Co-60 gamma source at Nuclear Institute for Food and Agriculture (NIFA), Peshawar, with dose rate 200 Gy h^{-1} . The $25 \text{ mL } 0.5 \text{ mmol L}^{-1}$ aqueous solutions of phenols were irradiated for the desired dose. The used Co-60 source was the only accessible source for said activity.

2.4 HPLC system

The HPLC solvent delivery system consisted of quaternary gradient pump K-1001, solvent organizer K-1500 and UV–Vis HPLC detector K-2501, were from Knauer, Germany. Injection loop of $20 \mu\text{L}$ was used in combination with Rheodyne injector 7725i. The phenols were monitored at 254 nm. The reversed phase column was Discovery C 18 from Supelco, USA. For data handling software Eurochrom 2000, basic edition V2.05 was used. Eluent was 80 % methanol–water with flow rate of 0.4 mL min^{-1} . The HPLC monitoring of the degraded 0.5 mmol L^{-1} of different phenols was carried out and compared to those of standard.

2.5 SEM analysis

The SEM analysis was performed using microscope LEO 440, Leica.

2.6 Computational studies

HyperChem software version 7.0 was used for theoretical calculations of charge density data while optimizing the geometry of the compounds.

3 Results and discussion

3.1 Electrooxidation of phenols: influence of concentration and pH and substituent position

The EC behavior of phenol and its chloro-substituted analogs on GCE has been reported elsewhere [16]. The phenolic compounds have strong tendency to adsorb on the electrode surface [17, 18]. In the previous work [18], an attempt was made to optimize the EC conditions to

overcome its polymerization. It was concluded that ~ 0.04 M BRB as background electrolyte, 0.1 mmol L^{-1} phenol, 50 mV s^{-1} scan rate, and 2.1 pH are most suitable conditions for effective electrooxidation of the phenols. The irreversible electron transfer (ET) heterogeneous rate constants were of the order of $10^{-2} \text{ cm s}^{-1}$ with diffusion coefficient of the order of $\sim 2.5\text{--}3.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [18]. Furthermore, it has been inferred from the data that the ET process is not a purely diffusion controlled rather it is a diffusion plus activation controlled reaction [16, 18]. Moreover, the influence of Cl substituent, at different positions in the phenol ring, on the voltammetric behavior will be presented.

The CV of the 2,4,6-TCP, for the effect of varied concentration is shown in Fig. 1a. Linear increase in current with the increase in concentration was found and the cyclic voltammogram remained irreversible. The observed adsorption of phenol on the electrode is because of the highly reactive nature of the electrochemically produced phenoxy radicals which in turn give new compounds by coupling with each other [18, 19]. However, it is relatively reduced for the substituted phenols as mentioned earlier [18]. Appearance of minor reduction waves, in the reverse scans for TCP, at sufficiently wide potential depicts its different behavior as compared to the phenol.

The effect of pH on peak positions and currents for TCP are presented in Fig. 1b. It is apparent, that there is a potential shift towards less positive value (from +0.8 to +0.58 V) while going from pH 2.1–5.5. The observed negative potential shift at high pH is attributed to the dominance of phenolate anion which converts to phenoxy radical; during the EC oxidation and gives a relatively symmetric peak. In acidic medium, EC oxidation of phenol occurs through phenoxonium cations, i.e., removal of proton followed by the removal of an electron to form phenoxy radicals [17, 20]. Higher is the concentration of phenolate anions more easily it will be electrooxidized [20].

The CV of 2-CP with varying number of cycles at 50 mV s^{-1} scan rate has been shown in Fig. 2a. The

decrease in the peak current was observed with each successive repeated cycle accompanied with a slight positive shift in the peak potential. It was attributed to strong adhesion of the oxidized 2-CP phenol with the electrode surface and was found dependent on its concentration and scan rate. On the other hand 3-CP (Fig. 2b) did not exhibit any minor reduction peak as appeared in 2-CP which reflects its slow reactivity. Moreover, for TCP with repeated cycles (Fig. 2c) there is an indication of the formation of EC intermediate (electrooxidative product) around +0.38 V. Percentage decreases in the peak currents from first to second CV cycle for different CPs are reported [18]. The percentage decrease in current from first to second cycle in the case of 2-CP is 25 % a bit lower to that of phenol 30 % and this decrease for 2,4,6-TCP becomes 21 % [18]. That indicates relatively low probability of the formation of polymeric products at the electrode surface in case of CPs. For phenol, all of the positions in the ring are vacant and the radical–radical or radical analyte joining probability of the resulting phenoxy radicals is higher. That is more obvious at higher concentrations and at lower scan rates. It can be interpreted that the electropolymerization causes a certain decrease in the peak current values while the formation of electroactive intermediate(s) results into the appearance of new peaks in the voltammogram.

The electrooxidation of 2,4,6-TCP can help to understand the role of chlorine at *ortho* and *para* positions in the formation of new intermediates and polymeric products. First, that after reaching 5th or 6th repeated scan, there is no further decrease in the peak current. It may be mainly due to the blocking of *ortho* and *para* positions by a Cl substituent, the polymer structure formed on the surface of electrode is more asymmetric and hence more permeable for further electrooxidation of 2,4,6-TCP as compared to phenol and 3-CP. The second and more clear indication is the formation of new EC products thus exhibiting a lesser polymerization by having $\Delta E_p = (E_p^a - E_p^c) = 120\text{--}160 \text{ mV}$ (Fig. 2c). The concentration of these new intermediates goes on increasing with a continuous increase in the number of repeating scans.

Fig. 1 Cyclic voltammograms of 2,4,6-TCP with **a** varied concentrations at pH 2.1, **b** 0.1 mM concentration with varied pH, on GCE versus SCE, scan rate 50 mV s^{-1} in BRB

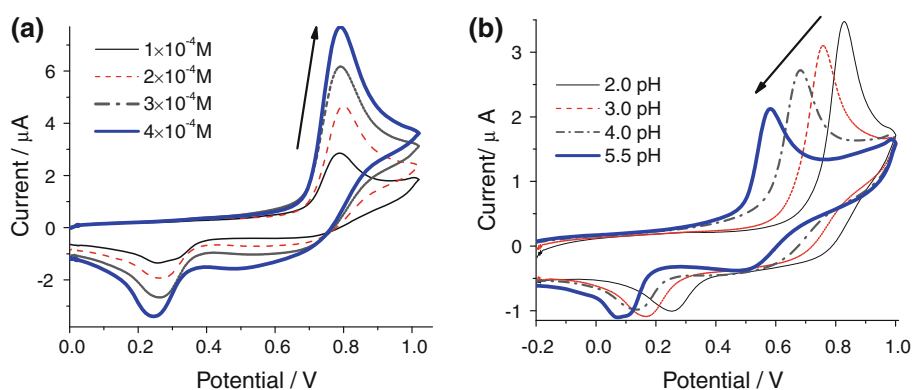
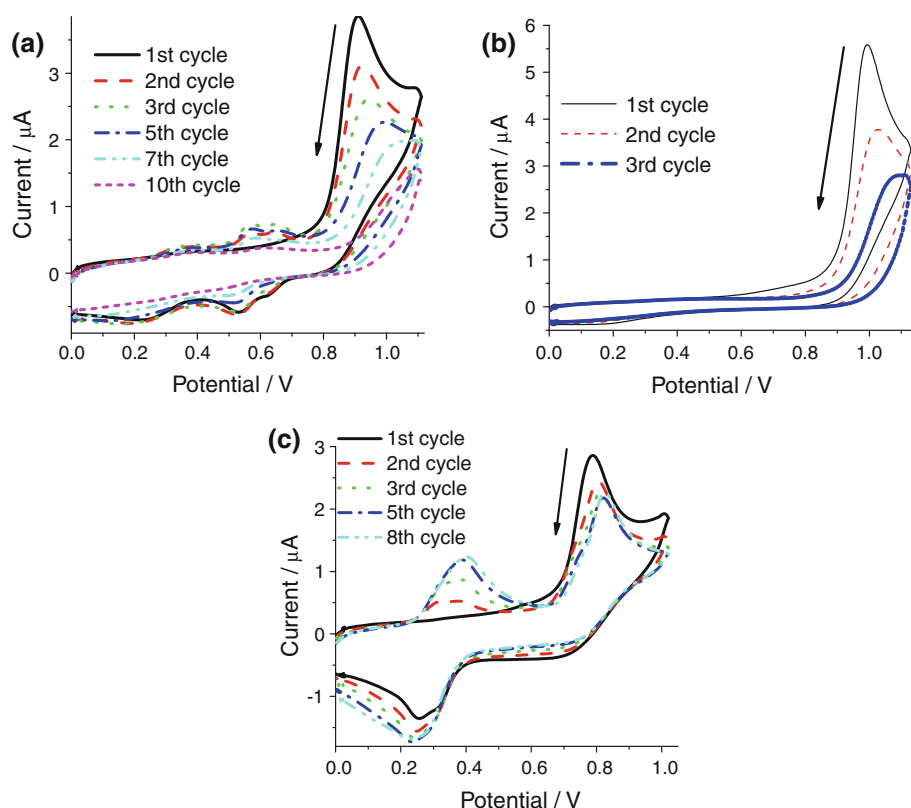


Fig. 2 The influence of repeated scanning for **a** 2-CP, **b** 3-CP, **c** 2,4,6-TCP, 0.1 mM each at pH 2.1, on GCE versus SCE, scan rate 50 mV s^{-1} in BRB



In the electrooxidation of 3-CP (Fig. 2b) there is neither a small shoulder in the reversal scan, as it appeared in the case of phenol and 2-CP, nor is any evidence of EC intermediates with the repetition of scans. However, the formation of polymeric products is prominent for 3-CP. This might be due to the fact that *meta* chlorine does not impart any resonance effect and only influences through negative inductive effect (electron withdrawing) and hence does not involve the resonance of negative charge present on the oxygen atom of the phenoxy radical. In case of a simple phenol, the negative charge on the phenoxy radical resonates over *ortho* and *para* positions with an equal ease. In the case of 2-CP, the inductive and resonance effects almost nullify each other and approximately similar is the case for 2,4,6-TCP. The stability of new intermediate species generally depends on the delocalization and rearrangement of the negative charges over various positions in the ring [20]. So, from the repeated CV of CPs it can be inferred that the resonance and inductive effects are important contributors in the formation of new EC intermediates other than the polymers as shown in Fig. 2.

3.2 Surface morphology of the coated GC electrode

The surface morphology of the working electrode before and after CV of phenol was investigated by SEM. Figure 3a shows the surface morphology of the active portion of the GCE (disk shaped) before the electrooxidation of phenol.

The homogeneous wavy-like appearance could be due to the inbuilt chemical composition of the working electrode. After phenol electrooxidation (Fig. 3b), the electrode surface has changed significantly and is partially covered due to the adsorbing nature of the newly produced species. Figure 3c, d with higher resolutions focus few macro molecules, particularly. The adsorption of these products makes the electrode surface impassive for further electrooxidation of phenol, and therefore, their removal is imperative to reactivate the electrode surface. As far as the chemical nature of these species is concerned, there are two views. One possibility is the electropolymerization of the phenol, highly probable in concentrated solutions; the other is direct mineralization [17, 18]. In this study, the SEM data is used as a physical evidence to show the electrode fouling and thus complement/predict the voltammetric findings of phenols. For example, the intensity of surface fouling is expectedly lower in case of chloro-substituted phenols. An interesting study could be the in detail investigation of the adsorbed species, on the working electrode surface, during the electrooxidation of different phenols.

3.3 Gamma radiolytic degradation of phenols: CV monitoring

The primary objective of this EC study was to monitor the γ -radiolytic degradation trend of the targeted compounds

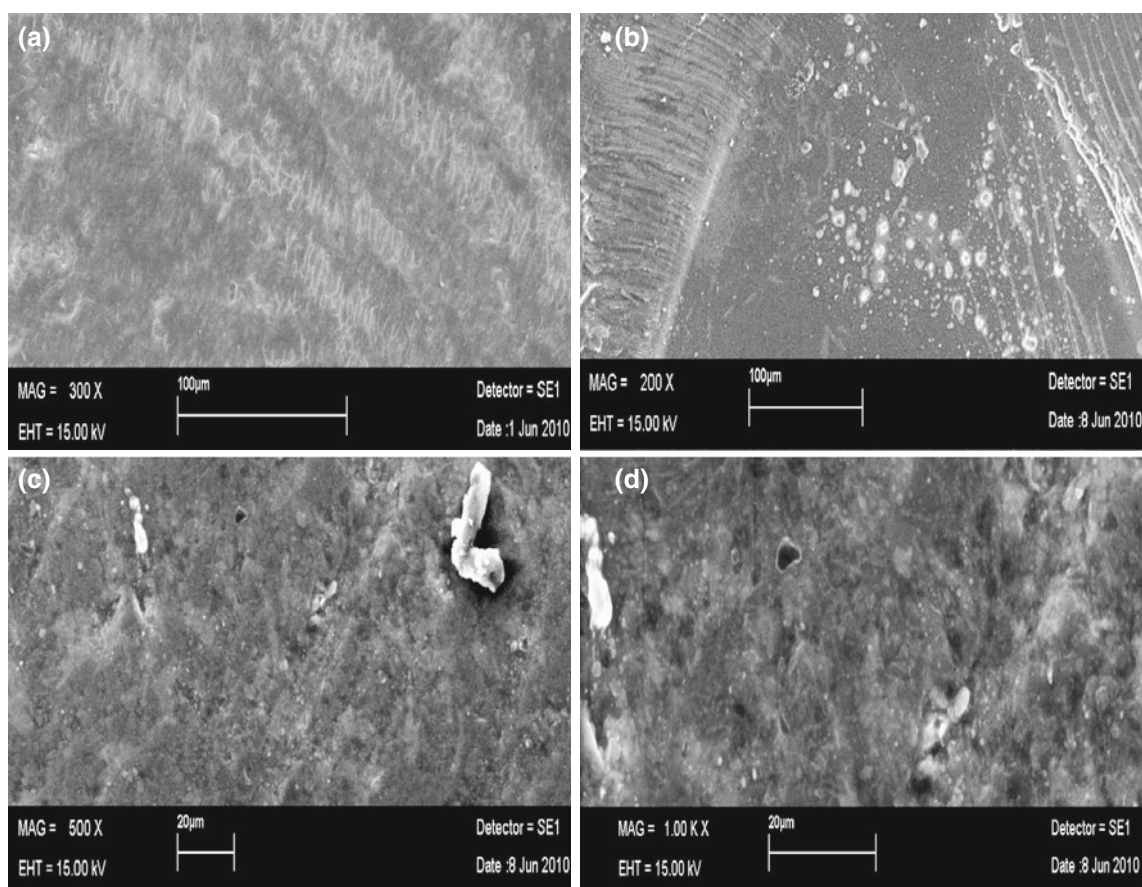
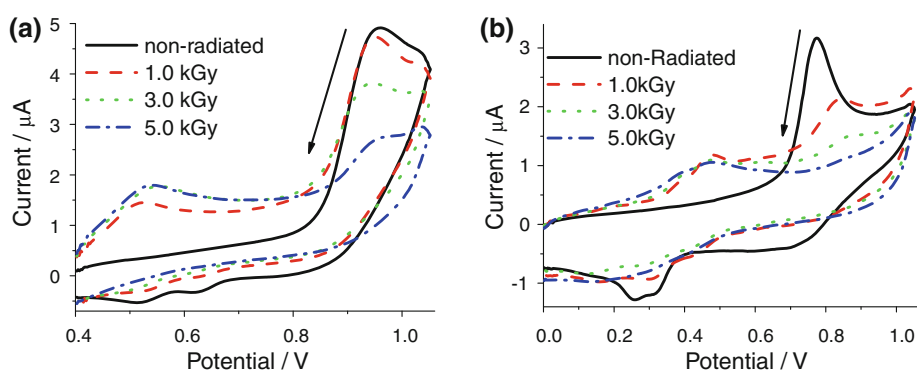


Fig. 3 SEM images of the GCE with different resolutions; **a** before, **b–d** after EC oxidation of phenol

Fig. 4 Cyclic voltammetric response before and after γ -radiolytic degradation. **a** Phenol, **b** 2,4,6-TCP, each 0.1 mM, on GCE versus SCE, scan rate 50 mV s⁻¹ in BRB



and wherefrom check the suitability and efficiency of the EC technique in comparison to established methods, such as spectrophotometry and HPLC. Aqueous solutions of 0.5 mmol L⁻¹ phenols irradiated with accumulative doses of 1, 2, 3, 4, and 5 kGy were diluted in respective buffer to 0.1 mmol L⁻¹ for post γ -irradiated EC monitoring. Figure 4 illustrates the pre and post degradation CV patterns of 0.1 mmol L⁻¹ concentrations of the phenol and TCP. The peak currents decreased owing to the decrease in the concentrations of the respective phenols and also there was an indication of the formation of the γ -irradiated

degradation products, giving a considerable variation in the currents between the potential ranges of 0.4–0.6 V. The peaks for the degradation products appeared at less positive potentials indicating the easy electrooxidation of degradation products in comparison to the parent species and hence thermodynamically more feasible.

The decrease in peak currents was used to determine the corresponding decrease in the concentration of the compound. The data is shown in Tables 1 and 2. The radiolytic yield, G value was calculated from Eq. 1 [21], and it is defined as the number of molecules degraded per 100 eV,

which is a direct measure of the extent of pollutant degradation.

$$G = [\Delta R]N_A/D (6.24 \times 10^{17}) \quad (1)$$

where $[\Delta R]$ is the difference in concentration of the given compound before and after irradiation, N_A is the Avogadro's number (i.e., 6.023×10^{23}), D is the dose level in k rads and 6.24×10^{17} is the conversion factor from k rads to 100 eV L^{-1} , where $100 \text{ rad} = 1 \text{ Gy}$.

From the comparison of the G values in Table 2, the extent of degradation of the phenols can be estimated under the same applied doses. In addition, a difference in the G values while varying γ -doses, from lower to higher values can be useful to determine some other interesting aspects of the process. From Table 1, it can be noted that the degradation efficiencies increase with the increased γ -dose, while radiolytic yields (G values) decrease with an increase in the dose level because more energy is being provided to the compounds to be degraded. At higher doses relatively less number of molecules is exposed to the radiations because some of them have already been degraded at lower doses. Moreover, at lower doses, some intermediate species are expected to be formed and they also get a chance to be exposed to the radiations at higher levels of γ -dose and hence are capable of being oxidized to new intermediate species. So, the G values decrease and the degradation efficiencies increase with an increment in the dose of γ -radiations.

Table 1 A comparison of γ -radiolytic degradation efficiencies of phenol by CV and HPLC

γ -Dose (kGy)	Degradation efficiency (% age)		G value	
	CV	HPLC	CV	HPLC
1	24.80	22.40	0.24	1.08
2	33.13	32.40	0.16	0.78
3	45.53	45.40	0.15	0.73
4	55.69	59.00	0.13	0.71
5	61.58	74.00	0.12	0.71

Initial concentrations of phenol for CV and HPLC were 0.1 and 0.5 mmol L^{-1} , respectively

Table 2 Monitoring of removal efficiencies and G values of the phenols at 5.0 kGy by CV and HPLC

Compounds	Degradation efficiency (% age)		G value	
	^a CV	^b HPLC	CV	HPLC
Phenol	61.58	74.00	0.12	0.71
2-Chlorophenol	70.47	86.6	0.14	0.83
2,4,6-Trichlorophenol	79.50	96.4	0.15	0.93

^a 0.1 mmol L^{-1} initial concentration of the phenol

^b 0.5 mmol L^{-1} initial concentration of the phenol

3.4 Monitoring of the degradation by HPLC

HPLC monitoring was carried out to examine the formation of degradation products by radiolysis of different phenols. The results are interpreted to study the γ -dose effect on the degradation efficiencies and radiolytic yields (G values) of the selected phenols and were compared to those found earlier from the voltammetric data. The effect of chlorine as substituents, at different positions of phenol, on the degradation has also been investigated.

The γ -dose effect was monitored from 1 to 5 kGy for each 0.5 mmol L^{-1} of phenol, 2-CP, and 2,4,6-TCP. The HPLC chromatograms in Fig. 5 show that by increasing dose, the concentration of degradation products formed increases while that of parent compound decreases. The peak for 2,4,6-TCP almost disappeared for a 5 kGy accumulative dose and thus indicating its almost complete degradation. The peaks due to the newly formed intermediate products became even more prominent for relatively higher γ -dose as shown in Fig. 5.

From the observed degradation trend the corresponding degradation efficiencies were calculated using area under the peaks and Eq. 1. The results are compiled in Tables 1 and 2. A similar pattern for degradation efficiencies and G values at varied γ -doses has been observed as it was attained by CV. However, in case of HPLC measurements the obtained G values are higher in comparison to those obtained by voltammetric data mainly due to five times higher than the phenols concentrations for HPLC studies. Consequently the substrate concentration-dependent G value is higher. The G value decreases with an increase in the dose for all of the phenols (Table 2) that is in agreement to earlier findings by voltammetry.

3.5 Theoretical charge densities and molecular mechanism of radiolytic degradation

The radiolysis of water leads to the formation of very reactive primary radicals (H , e_{aq}^- , OH) and molecular products H_2 , H_2O_2 [22]. It is generally accepted opinion that phenol degradation starts with these water radiolysis products [23]. Among these reactive species OH radicals are the principle oxidants, while the reducing species (e_{aq}^- , H) are converted into ineffective oxidizing agents like HO_2 and O_2 in the presence of air and are thus generally ignored in the oxidative degradation process [24].

OH radicals are strong electrophiles and can attack at various electron rich sites usually present in the aromatic ring of phenols. In order to find out the probable electron rich sites in the aromatic rings of different phenols, theoretical calculations have been carried out by HyperChem program version 7.0. A comparison of the resulting negative charges obtained due to simulation at *ortho*, *meta*, and *para* positions

Fig. 5 γ -Radiolytic degradation monitoring by HPLC of 2,4,6-TCP **a** standard solution 2.5×10^{-4} M, **b–d** 5.0×10^{-4} M exposed to 1, 3, and 5 kGy γ -doses, respectively

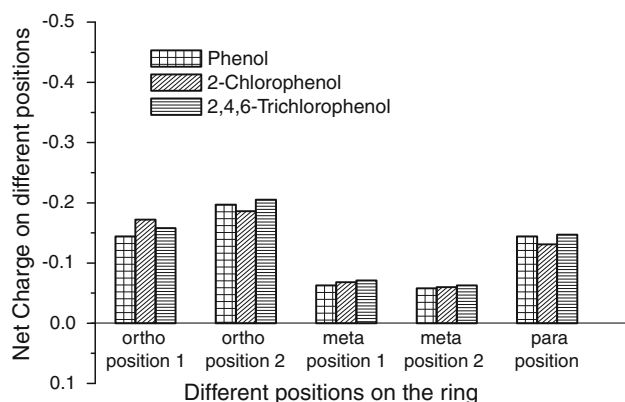
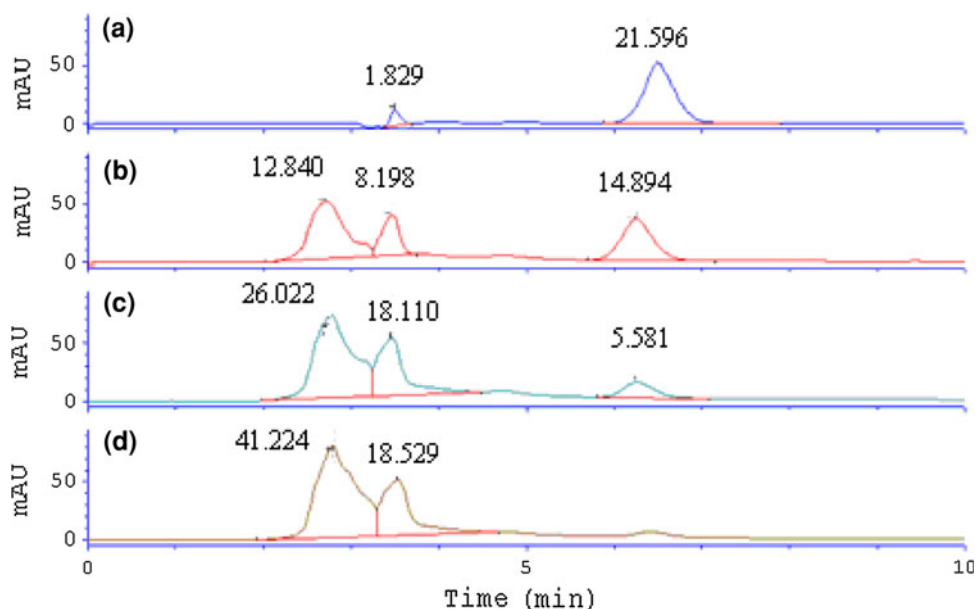


Fig. 6 Net negative charge densities at different positions of the aromatic ring of the phenols

of the investigated phenols have been presented in Fig. 6. This figure depicts that more negative charges reside over *ortho* and *para* positions. In the case of phenol, 2-CP and 2,4,6-TCP three to four times smaller negative charge reside over meta positions as compared to *ortho* and *para* positions. Therefore, the hydroxyl radical most probably attack at *ortho* and *para* positions. These transients formed due to the radiolysis of water preferably attacking at *ortho* and *para* positions and break them down into smaller fragments or some other intermediates. The resulting main transients could be OH adducts as reported earlier in the literature [25].

4 Conclusions

In the present studies, some CPs were electrochemically investigated before and after γ -radiolytic degradation. It

was found that the phenol degradation is γ -dose dependent and the G value decreases with an increase in γ -dose, indicating its substrate concentration dependence. Chloro substitution not only facilitates the electrooxidation but also favors its radiolytic degradation. The radiolytic degradation efficiencies and G values calculated from the CV were found in good agreement to that obtained from HPLC. The findings reveal that the CV technique can be used as an additional and efficient tool to monitor γ -radiolysis of the organic pollutants.

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